Chemical Engineering Journal 149 (2009) 463–472

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Scentfashion®: Microencapsulated perfumes for textile application

S.N. Rodrigues [a], I.M. Martins [a], I.P. Fernandes [b], P.B. Gomes [a,c], V.G. Mata [c], M.F. Barreiro [b], A.E. Rodrigues [a,*]

[a] *Laboratory of Separation and Reaction Engineering, Associate Laboratory LSRE/LCM, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr Roberto Frias, 4200-465 Porto, Portugal*
[b] *Laboratory of Separation and Reaction Engineering, Associate Laboratory LSRE/LCM, Bragança Polytechnic Institute, Campus Santa Apolónia Ap 1134, 5301-857 Bragança, Portugal*
[c] *I-SENSIS Lda., CTCP, Rua de Fundões – Devesa Velha, 3700-121 S. João da Madeira, Portugal*

ARTICLE INFO

Article history:
Received 13 October 2008
Received in revised form 11 February 2009
Accepted 13 February 2009

Keywords:
Microencapsulation
Perfumes
Polyurethane urea microcapsules
Textile application

ABSTRACT

This work is a contribution to the introduction of emergent technologies in the textile sector, namely the microencapsulation of fragrances and its application to obtain added-value products.

Interfacial polymerization was used to produce polyurethane/urea (PUU) microcapsules with a perfume for industrial application on textile substrate having in view man suits production.

The extent of reaction of PUU microcapsules formation was followed by Fourier transform infrared spectroscopy. Size distribution and morphology of the produced microcapsules were studied using particle size analysis, optical microscopy and scanning electron microscopy.

Impregnation on textile substrates was tested both at laboratory level and at industrial scale. The fragrance release from textile substrates was measured with headspace chromatography. The content of microcapsules was released with light abrasion to simulate day-to-day wear, and fabrics impregnated at laboratory scale have survived to 9000 abrasion cycles. Microcapsules have continued to release aroma up to five dry cleaning washing cycles.

1. Introduction

In this paper we report the preparation, via interfacial polymerization, of PUU microcapsules [1] containing perfume and its subsequent application on fabrics. It is an example of product engineering [2–5] approach starting from market *needs* (perfumed suits for man) up to the *manufacture* of microcapsules after *selection* of a microencapsulation technique and shell material type among various possibilities.

Polyurethanes have been used in a variety of applications since they are one of the most versatile materials in the world today. These polymers represent an important class of both thermoplastics and thermoset polymers. Due to its excellent physical properties and good compatibility, polyurethanes are used in several industrial applications (coatings, adhesives, sealants and elastomers used on floors and automotive interiors) and also for the development of biomedical devices or drug delivery systems [6].

Nowadays, scientific advance is being used for the development of innovative textile products. Insect repellents [7], anti-cellulite treatments, long-lasting fragrances and skin softeners [8–10], medical applications such as antibiotics, hormones and other drugs [11–13] and antimicrobial agents for medical textiles [14,15] are some applications for which clothing manufacturers are applying to add value to the products. In particular, finishing a textile with a fragrance is an important commercial target and an engineering challenge [16]. Developing new products with high added-value properties increases competitiveness, improves market dynamics and may lead to economic growth of industry [17].

Encapsulation techniques allow an opportunity for variable fragrant finishing that can favour its durability [18]. This innovative technology makes use of microcapsules which act as small containers of liquids to be released from the inner core under controlled conditions to address a specific purpose [19].

There are a number of patents related to microencapsulation of flavours and fragrances with different applications. Table 1 presents a summary of the patents associated to textile applications.

In this work the perfume formulation was performed taking into account the target market and the type of textile substrate for man suits. In the perfume conception special attention was given to the performance of different components of perfume. The perfume ingredients are classified in three types of perfumed notes according to their volatility: (i) top notes: more volatile components; they are noticed after the application of the perfume and last for a short

* Corresponding author. Tel.: +351 225 081 671; fax: +351 225 081 674.
E-mail address: arodrig@fe.up.pt (A.E. Rodrigues).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.02.021

Table 1
Patented processes for microencapsulation of flavours and fragrances and applications in textile industry.

Arcade, Inc. (1991) [20]	Methods for preparing microcapsules with perfume oil. Microcapsule wall is made of polymeric material of ethyl cellulose.
Aero, Kemicna, Graficna in Papirna Industrija, D.O.O. (1996) [21]	Preparation of microcapsule (melamine–formaldehyde or urea–formaldehyde) emulsion, coating and impregnation of carrier with microencapsulated scents.
Givaudan Roure (International) SA (2000) [22]	A coacervation procedure of encapsulating an amphiphilic flavour or fragrance using hydrogel shell and an oil core.
3M Innovative properties company (2001) [23]	Methods for production microbeads of hydrogel (polysaccharides or synthetic polymers) to immobilize water soluble and water insoluble active principles (oils, fragrances and agricultural chemicals such as pheromones, insecticides).
Sara Lee Corporation (2002) [24]	Processes for applying microcapsules to textile (nylon) materials.
Bayer Corporation (2002) [25]	Method for the production of leather or textile substrates with scent-containing microcapsules. The microcapsule wall contains reaction products of guanidine, polyamides and polyisocyanates.
Firmenich SA (2003) [26]	Method for the preparation of extruded delivery systems advantageous for the controlled released of an active hydrophobic principle such as flavours or perfumes.
Centre National De La Recherche Scientifique (CNRS) (2004) [27]	Microencapsulation techniques (coacervation, polymerization or polycondensation) to encapsulate oil substances or sugars. The microcapsules can be used in therapeutics or in cosmetics.
The Hong Kong Polytechnic University (2004) [28]	Microencapsulation of phase-change paraffins using melamine–formaldehyde shell. The microcapsules were coated on textile fabrics to improve thermal regulation function.
BASF Aktiengesellschaft (2006) [29]	Production of microcapsules dispersion; the capsule core comprises a water soluble organic substance, such as water soluble dyes and the capsule wall is composed basically of polyureas.
Firmenich (2006) [30]	Method for producing microcapsules of 40–1000 nm containing fragrances: the shell is made by reactions between isocyanates, diols and diamines.
Firmenich (2007) [31]	Perfuming ingredient in microcapsules with a guanidine based poly-urea or poly-urea/polyurethane wall.

time (30 s to some minutes). Examples are: lemon, mint and grass; (ii) middle notes: these fragrances give the main character to a perfume; they are detected right after the disappearance of top notes and can last some hours. Examples include flower and fruity odours; and (iii) base notes: these fragrances can last for many hours and are used as fixative of the whole perfume, since they lower the volatility of top and middle notes. Examples are woody, musk and vanilla aromas.

The pyramid structure of a perfume (Fig. 1) suggested by Carles [32] is divided in three parts; each one representing top, middle and base notes. The recommended Carles ratios for each fragrant note are: top, 15–20%; middle, 30–40%; and base, 45–55% [33–34].

Adding fragrances to textiles has been carried out for a long time in the form of fabric conditioners in the wash and during tumble-drying. However, no matter the quality of the technique used to incorporate the fragrance, its effect is relatively short-lived, only surviving one or two wash cycles [35]. The encapsulated active agent is released from the textile by breaking the shell; when the size of microcapsules is higher, easier is the release of fragrance.

The microcapsules can be applied by stamping works, exhaustion dyeing, impregnation, spraying and coating or by direct incorporation in the fibre without modifying its touch and colour. In this work, microcapsules were impregnated into the fabrics on the finishing process using a foulard as represented on Fig. 2, followed by drying and curing steps.

A crosslinking agent is required for the impregnation of microcapsules in the fabrics. This is the component that forms the continuous film, adherent to the substrate, and holds the microcapsules in the fabric [36]. Crosslinking agents can be acrylic, polyurethane, silica, etc. Its function is to fix the microcapsules in the fabric preventing them to be loose during laundering. Several kinds of fabrics can be impregnated with microcapsules as silk, cotton or synthetic fibres (polyamide or polyester).

In a process for applying microcapsules to textile materials, microcapsules can be initially introduced in the textile material without a crosslinking agent; a dispersant is introduced to disperse the microcapsules around and through the textile material, and thereafter the crosslinking agent is added to promote the adhesion of microcapsules to the textile material [31]. Alternatively, microcapsules can be applied during the finishing process of textiles fabrication using a foulard in which the textile to be treated is impregnated by means of a finishing bath containing microcapsules, a softener and a self-crosslinking agent [2]. Taking into account the type of final application, the microcapsules have to fulfil specific requirements, such as resistance to abrasion and to dry cleaning wash cycles [35].

In this work, we have provided a strategy by firstly selecting a perfume composition without amine and hydroxyl groups (confirmed by FTIR analysis of perfume) and secondly by using two distinct amines (EDA followed by HYD, a more reactive amine) to

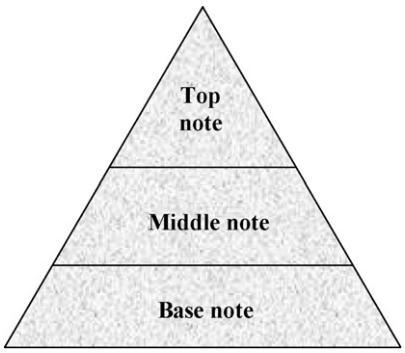

Fig. 1. Classical perfume pyramid structure.

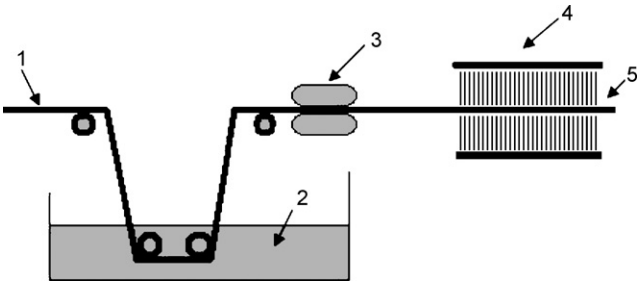

Fig. 2. Schematic representation of the microcapsules application process in fabrics using a foulard. (1) Untreated fabric; (2) microcapsules bath; (3) squeezing zone; (4) drying and curing; (5) fabric treated containing microcapsules.

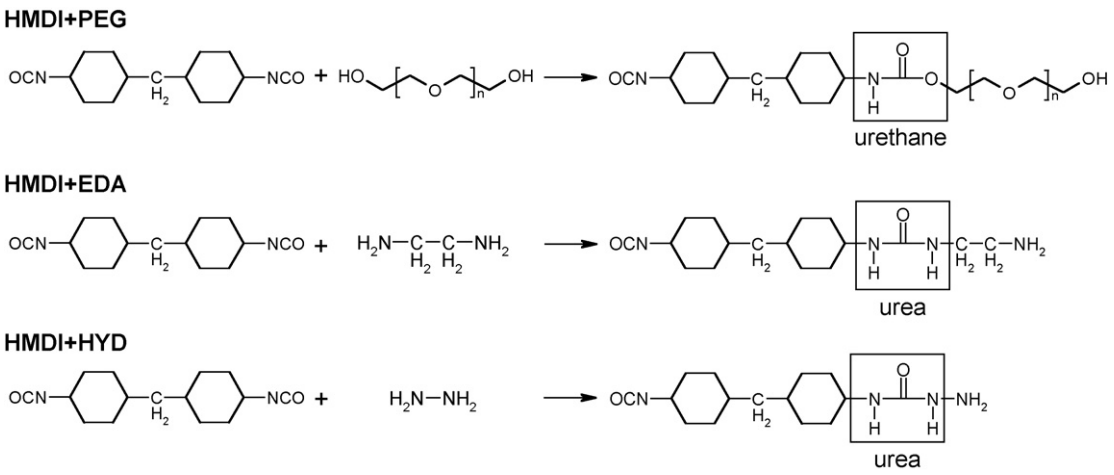

Fig. 3. Reactions of formation of polyurethane and urea shell of microcapsules.

guarantee total isocyanate consumption (confirmed by FTIR analysis of shell material) during the polymerization reaction. In spite of the above limitations, the process presented in this work is a step forward on perfume microencapsulation technology and provides a viable alternative to phenol-formaldehyde or melamine-formaldehyde systems traditionally used in textile applications. Moreover, polyurethanes–urea (PUU) system comes out as a green solution. They are known as versatile polymer systems which can be custom-made from a large selection of raw materials in order achieve the desired physical chemical and mechanical properties. The only negative aspect is that polyurethane–urea systems must be designed and optimized taking into consideration the particularities of the active principle to be encapsulated.

The objective of this work is to study the production and application of PUU microcapsules containing perfume, in the textile industry. It involves the production and characterization of microcapsules, impregnation of textile substrate at laboratory and industrial scale, and final product characterization in terms of resistance to abrasion and to dry cleaning cycles.

2. Materials and methods

The materials used for the formulation of perfume were: limonene (lemon scent – LMN) (Sigma–Aldrich), methyl cedryl ketone (vetiver scent – MCK) (Sigma–Aldrich), methyl dihydrojasmonate (jasmine scent – MJD) (Sigma–Aldrich) and 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-enzopyran solution (galaxolide); 50% in diethyl phthalate (dep) (musk scent) (Sigma–Aldrich).

For the preparation of PUU microcapsules the reactants were: hexamethylene-1,6-diisocyanate (HMDI) (Bayer, Desmodur W) as the isocyanate; dibutyltin dilaurate (DBDTL) (Sigma–Aldrich) as the catalyst; polyethylene glycol 400 (PEG 400) (Sigma–Aldrich) as the polyol; ethylenediamine (EDA) (Panreac) as amine I; hydrazine monohydrate (HYD) (Sigma–Aldrich) as amine II; polyvinyl alcohol (PVA) (Celanese Chemicals, Celvol 840) as protective colloid and Triton CA (Dow Company) as emulsifier.

For the impregnation of the textile fabrics with PUU microcapsules using the foulard, the aqueous bath was prepared by adding microcapsules, a softener (Perisoft Nano, Bayer) and a polyether polyurethane self-crosslinking agent (Baypret USV, Bayer).

All reagents were used as received without any further purification.

2.1. Preparation of PUU microcapsules

PUU microcapsules were prepared by interfacial polymerization. The organic phase (OP) was formed by mixing the perfume and HMDI. The first aqueous phase (AP1) was constituted by water and PVA (used to stabilize the droplets and thereafter set up the microcapsules particle size distribution). Emulsion was formed by adding OP into AP1. Emulsification was performed at 11,000 rpm during 3 min with an ultraturrax (IKA T25 digital). Subsequently, a second aqueous phase (AP2), constituted by water, polyol (PEG 400) and catalyst (DBTDL), was prepared and transferred to the previously mentioned emulsion to form the polyurethane (PU) wall. Interfacial polymerization was performed in a batch reactor (IKA LR-2.ST) at 80 °C using a stirring rate of 100 rpm during 1 h. After this time period, a third aqueous phase (AP3: water and EDA) was added to proceed with urea formation. This stage takes 1 h. Since the reaction with EDA presents incomplete isocyanate conversion, a final aqueous phase (AP4) containing a more reactive amine (HYD) was added and let to react during 1 h. Using this strategy a complete isocyanate conversion was achieved.

The reactions involved on the formation of polyurethane and urea shell are shown in Fig. 3. The amount of the several phases identified in the text (OP, AP1, AP2, AP3 and AP4) was included in a Table 2.

Table 2 shows the chemical system and the composition of oil and aqueous phases used to prepare the PUU microcapsules.

Table 2
Chemical system and composition of oil and aqueous phases.

Phase	Composition							
	Perfume (ml)	Water (ml)	HMDI (ml)	PVA (g)	PEG400 (ml)	DBTDL (ml)	EDA (ml)	HYD (ml)
OP	200		60					
AP1		1000		16.8		2.0		
AP2		200			92			
AP3		80					16	
AP4		40						5.8

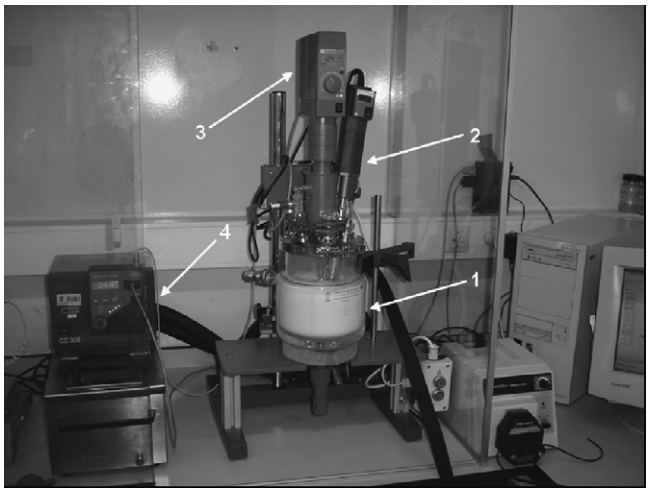

Fig. 4. Experimental set-up for the production of microcapsules by interfacial polymerization: (1) reactor vessel; (2) ultraturrax; (3) overhead stirring drive and (4) thermostatic bath.

The strategy used to cover the perfume with a PUU shell material uses NCO:OH:EDA-NH_2:HYD-NH_2 molar ratios of 1:1:1:0.5 which means that we are working with a 2.5× total excess of reactive groups (hydroxyls plus amine groups) relative to the isocyanate groups. Excess of reactants was thereafter removed by washing the microcapsules before storage. The complete experimental set-up for the production of microcapsules is shown in Fig. 4.

The obtained microcapsules were firstly washed with an ethanol solution (30%, v/v) followed by a centrifugation stage at 2400 rpm during 3 min. Thereafter the recovered microcapsules were subjected twice to a washing cycle with distilled water followed by centrifugation under the previously defined operational conditions. The final microcapsules were stored in an aqueous solution containing an emulsifier (Triton CA) to prevent the formation of agglomerates and increase microcapsules water compatibility.

2.2. Preparation of perfume

Several perfume formulations were developed and a panellist was used to choose the most attractive fragrance having in view the target-market: high quality man suits. The chosen fragrance belongs to the floral-woody-musk family and it was prepared with limonene, methyl dihydrojasmonate, methyl cedryl ketone and galaxolide (see Table 3).

The proportion of the fragrant compounds in this formulation was chosen using perfumery rules, and in particular, the scientific methodology PTD – Perfumery Ternary Diagram® developed in our laboratory by Mata et al. [37]. As a result, this formulation represents a typical perfume, having a highly volatile top note – LMN – which is noticeable when smelling directly from the solution or until some minutes after application. It means that the odour value (defined as the ratio of gas phase concentration and odour threshold) of the top note is higher than that of the middle and base notes. The middle note – MJD – is noticeable only after application and after the top note has disappeared; that is, because of the decrease in the concentration of the top note, the odour value of the middle note becomes higher than that of the top note. Finally, the base notes – MCK and MUSK – will be smelled after the middle note has disappeared.

Table 3
Floral-Woody-Musk fragrance compounds.

Fragrance note	Component	Odor	Liquid phase composition (wt%)
Top note	Limonene (LMN)	Lemon	19.51
Middle note	Methyl dihydrojasmonate (MJD)	Jasmine	35.67
Base notes	Methyl cedryl ketone (MCK)	Vetiver	35.67
	Galaxolide (musk)	Musk	9.15

The odour threshold of MCK was not available in the literature and therefore it was determined in our laboratory using an Olfatometer Ecoma model T07 (Germany). The detailed protocol is described in previous work by Gomes et al. [38].

Table 4 shows the molecular weight, vapour pressure and odour threshold for the components of the perfume. This information is necessary to map the Perfumery Ternary Diagram.

2.3. Impregnation of microcapsules on textile substrate

Fabrics of wool/polyester with different grammages were impregnated with perfume microcapsules. Microcapsules were applied by a foulard at the finishing process of textile fabrication. The finishing bath was prepared according to the conditions of industrial textile impregnation process described previously by Rodrigues et al. [1]. Briefly, perfume microcapsules (50 g/L) were suspended in a 70 L bath containing softener at 10 g/L (Perisoft Nano, Bayer) and a self-crosslinking agent at 50 g/L (Baypret USV, Bayer). The foulard (3 rollers) was used at a working speed of 10 m/min with fabrics of different grammages and with 1.55 m width. The impregnated textile was dried for 3 min at 100 °C and thermofixed at 140 °C during 3 min.

2.4. Characterization

2.4.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were collected on a FTIR BOMEN (model MB 104) in transmittance mode using two techniques: (1) using a liquid cell (an Omnicell® from Specac) with NaCl crystals to record the perfume spectra, and (2) using KBr pellets with a sample concentration of 1% (w/w) to record the shell material spectra. Spectra were collected between 650 and 4000 cm^{-1} at a resolution of 4 cm^{-1} and co-adding forty eight scans.

2.4.2. Mean particle size and particle size distribution (laser dispersion)

The particle size distribution of the produced microcapsules were analyzed by laser dispersion using a Coulter LS230.

2.4.3. Optical microscopy

A Leica DM 2000 microscopy equipped with the software Leica Application Suite Interactive measurement was used to analyse microcapsules in solution. The samples were analysed using the transmitted light mode.

2.4.4. Scanning electron microscopy (SEM)

SEM was used to analyse microcapsules in the impregnated textile substrates. Textile samples were coated with a thin layer of sputtered gold prior to examination, using an Ion Sputter JEOL JFC 1100. Samples were observed using a scanning electron microscope JEOL JSM-6301S at 15 kV.

2.4.5. GC-FID-headspace

Gas chromatography was carried out using a Varian CP-3800 instrument equipped with a split/splitless injector, a CP-Wax 52 CB bonded fused silica polar column (50 m × 0.25 mm, 0.2 μm film thickness) and a Varian FID detector controlled by Saturn 2000 WS software. The carrier gas was helium He N60, at a constant flow rate of 1 ml/min. The oven temperature was programmed as follows: isothermal (50 °C) during 5 min, then increased from 50

Table 4
Floral-woody-musk fragrance: vapour pressure and threshold values of components.

Component	Molecular formula	Molecular weight (M_w) (g/mol)	Vapour prssure (P_i) (Pa)[a]	Odour threshold (g/m^3)
LMN	$C_{10}H_{16}$	136.2	20.5×10^{1}	2.5×10^{-3}[b]
MJD	$C_{13}H_{22}O_3$	226.31	9.5×10^{-2}	2.8×10^{-4}[c]
MCK	$C_{17}H_{26}0$	246.39	1.1×10^{-2}	3.8×10^{-5}[d]
Musk	$C_{18}H_{26}0$	258.4	5.5×10^{-2}	6.3×10^{-7}[e]

[a] From database ChemSpider™ [39].
[b] From Calkin and Jellinek [40].
[c] From Leffingwell [41].
[d] Obtained by measurement using an olfactometer in our laboratory.
[e] From Frater et al. [42].

to 200 °C at 2 °C/min and held isothermal (200 °C) during 25 min. The injector was set at 240 °C, with a split ratio of 1/50. The FID detector was maintained at 250 °C. For the headspace analysis, it was used a gastight syringe (SGE, 1 ml). The sampling volume injected was 0.5 ml of the headspace. The sample was injected manually into GC-FID-headspace at a rate of 0.1 ml/s. The syringe was flushed with air after the sampling to prevent carryover of the sample between analyses.

3. Results and discussion

3.1. Spectroscopic analysis

3.1.1. FTIR analysis

The objectives of these assays were mainly two: (1) Before encapsulation, analyze the composition of the created perfume in order to guarantee the absence of hydroxyl and/or amine groups. These chemical groups are reactive towards isocyanates thus can compete with the used monomers and modify the aromatic properties of the fragrance; and (2) after microcapsules production, analyze the composition of the formed shell material and confirm total isocyanate consumption. For that purpose, samples of microcapsules solution were let to dry overnight in an oven at 60 °C and thereafter crushed and dried again until constant weight was achieved. Finally, they were transferred to a desiccator until analysis. This procedure allows perfume evaporation thus enabling shell material analysis. Moderate temperatures were used in order to avoid shell material degradation.

Fig. 5 shows the obtained perfume spectrum. Among other particularities we were able to confirm the absence of hydroxyl groups (absence of a broad band in the region 3400-3300 cm^{-1}) and amine groups (absence of a band of medium intensity around 3400 cm^{-1}). The weak vibration centred approximately at 3460 cm^{-1} corresponds to a carbonyl overtone.

Fig. 6 shows the FTIR spectrum of the produced polyurethane–urea microcapsules. Several infrared vibrations, typical of polyurethane–urea systems, could be assigned. According to our previous work [1], and for the chemical system used, urea formation is favoured over urethane formation. The N–H stretching mode is assigned at 3367 cm^{-1}, the urea carbonyl at 1677 cm^{-1}, and the amide II and amide III vibration modes at 1557 and 1241 cm^{-1}, respectively. The vibration assigned at 1106 cm^{-1} corresponds to the ether group C–O–C stretching mode. The low intensity associated to this vibration indicates the low urethane character of the produced microcapsules, since it corresponds to the PEG 400 incorporation. C–H stretching vibrations are assigned at 2927 and 2860 cm^{-1}. The carbonyl assigned at 1741 cm^{-1} in Fig. 6, which could be confused with urethane formation, could be easily detected in the original perfume spectrum (more precisely it was due jasmine contamination). Nevertheless, it was possible to verify the absence of the peak at 2270 cm^{-1}, due to the isocyanate stretching vibration and thereafter confirm that all the HMDI was consumed completely through the reaction with PEG 400, EDA and HYD.

3.1.2. Particle size distribution

After production and storage of perfume microcapsules, the particle size distribution was measured by laser dispersion and quantified both relative to the total volume of particles (a) and to the total number of particles (b), as shown in Fig. 7. The microcapsules mean size (based on volume distribution) is 10 μm. It was observed

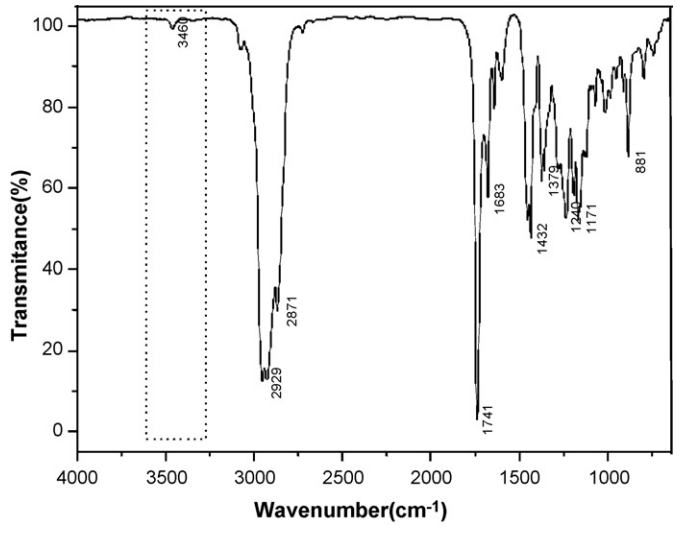

Fig. 5. FTIR spectrum of the encapsulated perfume with the following composition: limonene (19.51%), musk (9.15%), jasmine (35.67%) and vetiver (35.67%).

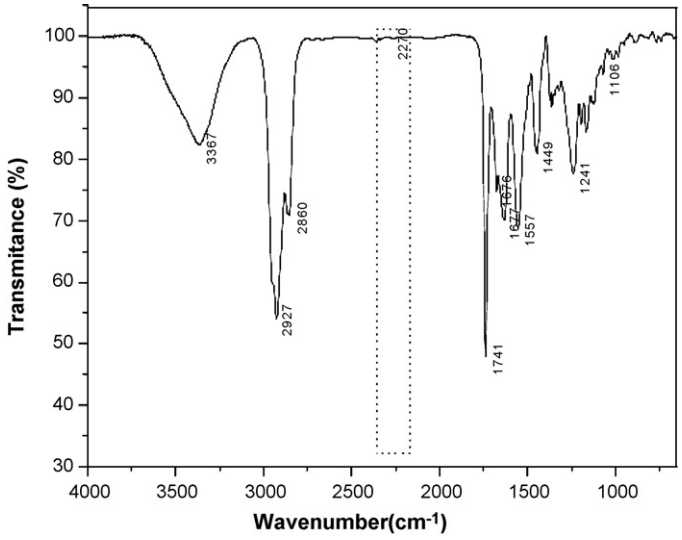

Fig. 6. FTIR spectrum of polyurethane–urea microcapsules with perfume.

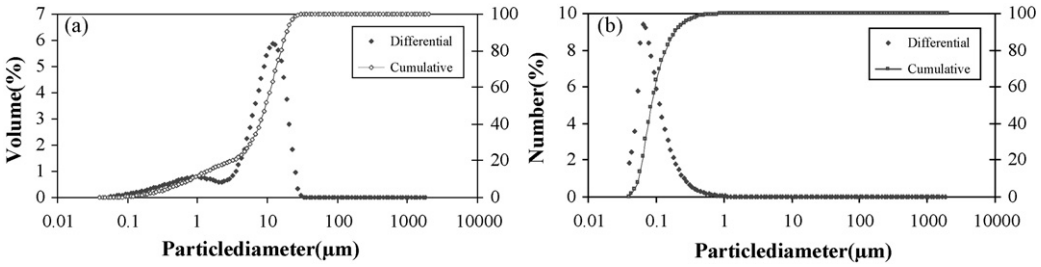

Fig. 7. Differential and cumulative particle size distribution in volume (a) and number (b) of polyurethane–urea microcapsules with perfume.

that 88% by volume of particles have diameters higher than 1 mm (12% < 1 mm), but this represents 1% of the particles by number (99% < 1 mm). This means that, even if a large number of microcapsules have small size, most of the perfume was encapsulated in larger particles.

3.1.3. Optical microscopy

The shape and morphology of the microcapsules is shown in Fig. 8. The optical microphotograph was taken after the polymerisation, washing and storage steps using bright field option at different magnifications, and it shows many small particles of 1 μm and large particles of about 10 μm. Fig. 8 shows the spherical morphology of perfume microcapsules and also confirms the bimodal size distribution.

3.1.4. Scanning electron microscopy (SEM)

Fig. 9 shows SEM photographs of fabric after being impregnated with microcapsules solutions in laboratory application. This figure confirmed that adhesion between textile fibre and microcapsules was effective and that the microcapsules are individually distributed without excessive agglomeration. The surface morphology of microcapsules was soft and smooth. It can be also observed that some microcapsules are broken and empty but still remain on the fabric protected by neighbouring fibres.

Fig. 10 shows SEM photographs of fabrics impregnated with perfume microcapsules in industrial application. It can be observed the adhesion of microcapsules to the fabrics, although their stability was apparently affected by the foulard process. During the industrial process microcapsules tend to agglomerate and to lose perfume, as it can be seen by the shape change of the microcapsules.

3.1.5. GC-FID-headspace

A sample for headspace analysis is normally prepared in a bottle containing both the sample and headspace (Fig. 11). The volatile components of the sample can be extracted and isolated in the headspace or gas phase in the bottle. Once the sample is introduced in the bottle that is thereafter closed, the volatile components spread out in the gas phase until headspace reaches a balance. Subsequently, 1 ml of the gas of headspace is collected and injected in the system of GC for the separation of all components.

Table 5 shows the comparison between the percentage of each component in the liquid phase and the percentage of each

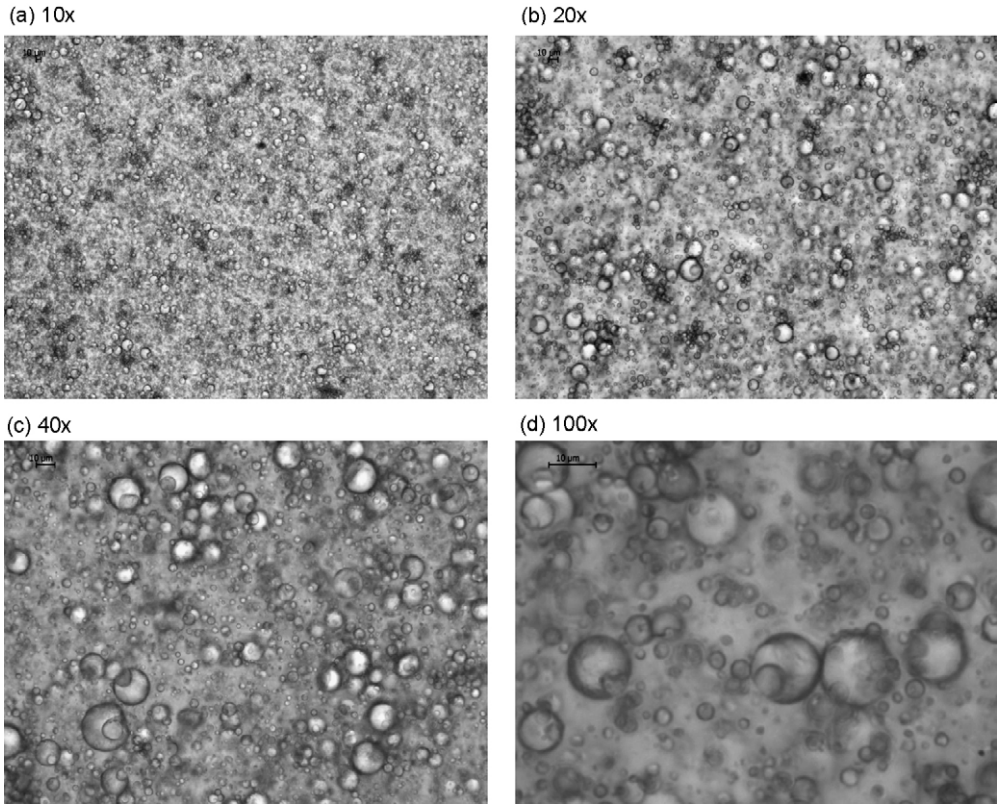

Fig. 8. Optical micrographs of microcapsules containing perfumes. (A)10×; (b)20×; (c)40×; (d)100×.

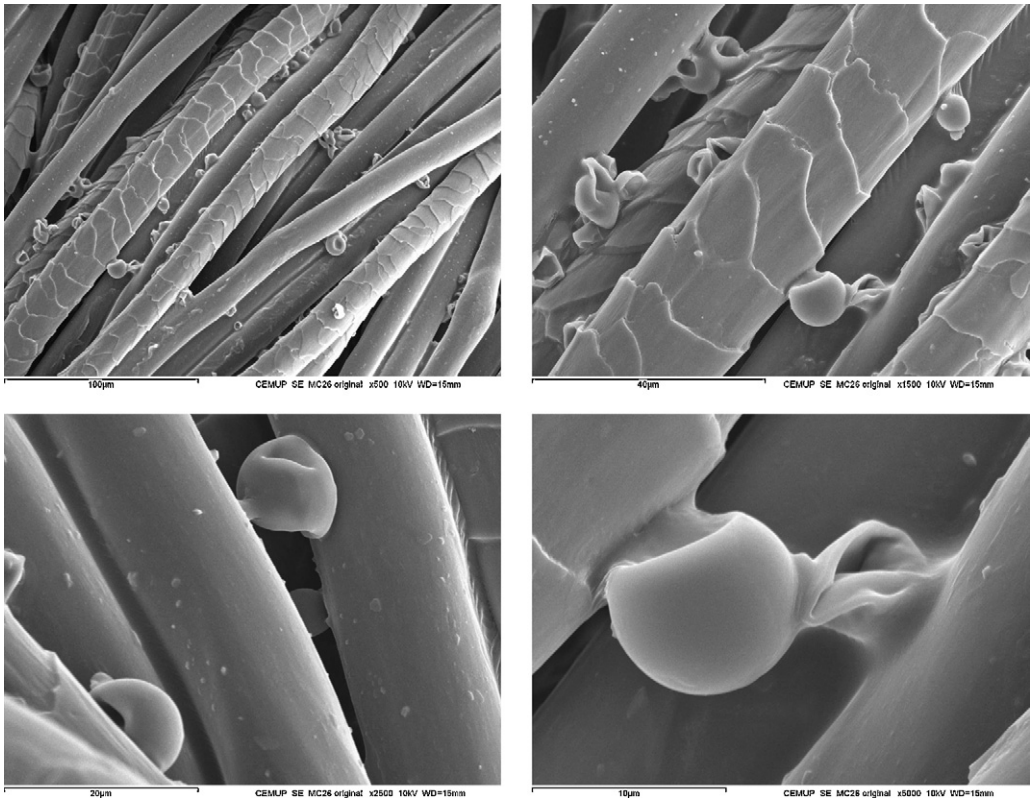

Fig. 9. SEM photographs of fabrics in laboratory application.

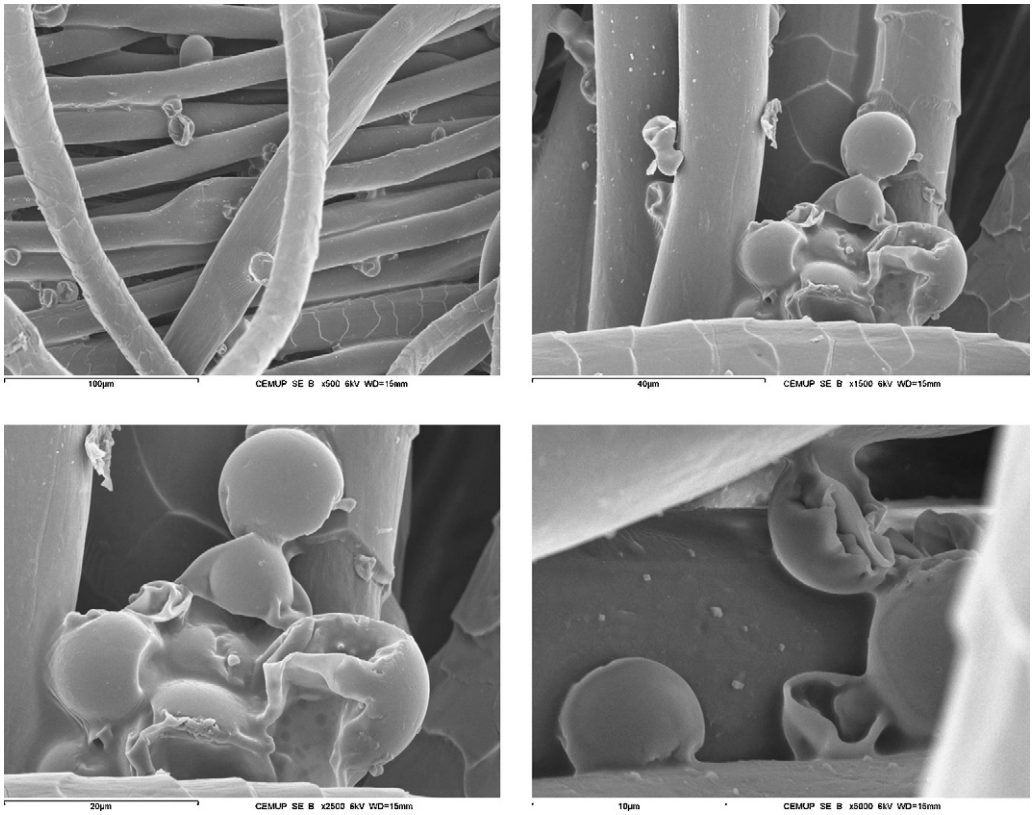

Fig. 10. SEM photographs of fabrics in industrial application.

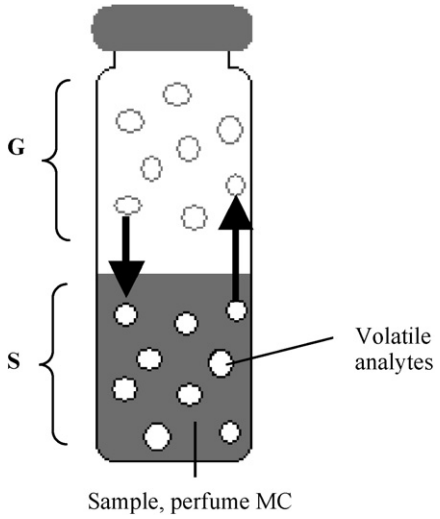

Fig. 11. Vial of headspace analysis; headspace phases: *G* = the gas phase (headspace); *S* = the sample phase.

Table 5
Fragrance components in liquid and gas phases.

Fragrance component	Liquid phase composition (wt%)	Gas phase composition (wt%)
Limonene (LMN)	19.51	97.68
Methyl dihydrojasmonate (MJD)	35.67	1.33
Methyl cedryl ketone (MCK)	35.67	0.43
Galaxolide (MUSK)	9.15	0.56

component in the gas phase of the fragrance released from the microcapsules.

Once limonene is the most volatile compound (top note), it appeared in the gas phase (headspace) at higher concentration, as it was expected. This way, although the perfume is composed by four components, the evaluation of the concentration of fragrance inside the microcapsules was based on the determination of limonene in the headspace.

The amount of perfume mass present on microcapsules was determined using the GC-FID-headspace technique. There were four peaks detected: the limonene peak appears at 12 min, the vetiver peak at 65 min, the jasmine peak at 69 min, and finally the musk peak at 72 min. The GC-headspace analysis allowed the quantification of the perfume present inside the microcapsules. The mass of encapsulated perfume has been calculated using a mass balance. The yield of encapsulation (percentage of perfume present inside microcapsules) was calculated based Eq. (1):

$$\text{Encapsulation efficiency}\ (\%) = \frac{m_{\text{total}} - m_{\text{out}}}{m_{\text{total}}} 100 \quad (1)$$

where m_{total} = amount of loaded perfume (g) and m_{out} = amount of nonencapsulated perfume (g).

The two phases obtained after separation by centrifugation (aqueous phase and microcapsules phase) were analysed in order to quantify the nonencapsulated perfume. 1 ml of the aqueous phase and 1 ml of the microcapsules phase were collected using a syringe equipped with a 0.45 μm pore size filter and thereafter analysed by GC-FID. The mass of encapsulated perfume was obtained by difference between the loaded original quantity and the nonencapsulated determined quantity. Table 6 shows total, encapsulated and nonencapsulated masses for each component of the perfume, the liquid phase composition and the encapsulation efficiency. The encapsulation efficiency accounts for 55% of the loaded perfume used in the encapsulation process".

Table 6 also shows that after encapsulation the proportion of the fragrant components in the liquid phase composition present some differences relative to the initial composition.

For headspace analysis, a procedure for the breakage of the microcapsules impregnated in the fabric was developed. It consists of isolating an impregnated fabric sample ($4 \times 4\,\text{cm}^2$) in a plastic bag ($12 \times 23\,\text{cm}^2$) (Fig. 12a) and breaking the microcapsules of the fabric without damage the plastic bag (Fig. 12b). Gas phase was left to equilibrate overnight and thereafter 1 ml was collected from the bag and analyzed by chromatography.

In the impregnated textiles in the industrial foulard 35 g of microcapsules per m^2 of fabric was used.

The amount of perfume applied in the impregnation is roughly 0.1 g perfume/g fabric. The fabric sample of 16 cm2 weights approximately 0.3 g after impregnation.

A perfume system consists of a complex fragrant liquid mixture and a corresponding air phase above it, the headspace, which we smell. The intensity of a fragrant compound i can be expressed in terms of its odor value OV_i, which is defined as:

$$\text{OV}_\text{i} = \frac{C_\text{i}^\text{g}}{\text{Thr}_i} \quad (2)$$

where C_i^g is the concentration of component i in the headspace and Thr_i is the threshold concentration of i in air.

The concentration of each perfume component in the fabric was compared with their threshold and the odor value was calculated. Comparing each component of the perfume with their odor threshold the results showed that musk and limonene scent odor values are the highest so these are the components that we smell more.

The effect of the number of dry washing cycles on the concentration of fragrance inside the microcapsules in the textile substrate impregnated at the laboratory scale was assessed by the determination of limonene in the headspace. Fig. 13 shows the relative amount of limonene in the headspace as a function of the number of dry washes.

As it can be seen, there is a decrease of limonene with the number of dry washing cycles. However, after five washes the lemon scent can still be detected due to the microencapsulation of the perfume.

The amount of limonene component in the fabric was compared with its threshold and the odor value was calculated. The results have shown that there is a decrease on odor value of 87% with five dry cleaning cycles.

Table 6
Total, encapsulated and nonencapsulated masses discriminated by perfume components and encapsulation efficiency.

Component	$\text{Mass}_{\text{initial}}$ (g)	$\text{Mass}_{\text{nonencapsulated}}$ * (g)	$\text{Mass}_{\text{encapsulated}}$ ** (g)	Liquid phase composition (wt%)	Encapsulation efficiency (%)
LMN	35.73	23.88	11.86	11.74	33.18
MCK	65.33	29.05	36.28	35.93	55.53
MJD	65.33	20.80	44.53	44.10	68.16
MUSK	16.76	8.44	8.32	8.24	49.64
Total	183.15	82.16	100.99	100.00	55.14

* Calculation based on GC-FID peak area.
** Obtained by difference between masstotal and massnonencapsulated.

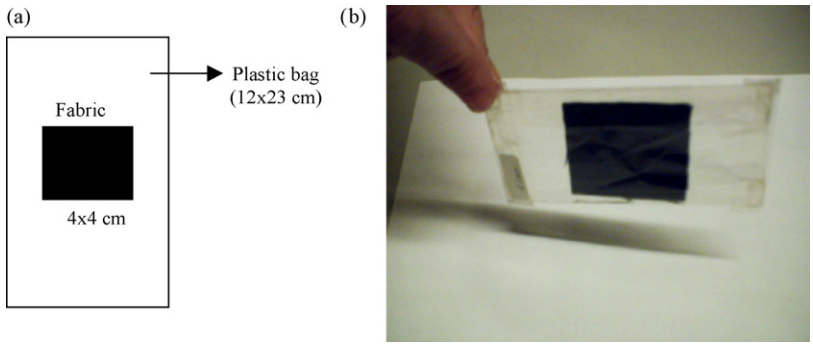

Fig. 12. Scheme of impregnated fabrics for GC-headspace analyse (a) and impregnated fabric isolated on plastic bag for GC headspace analyses (b).

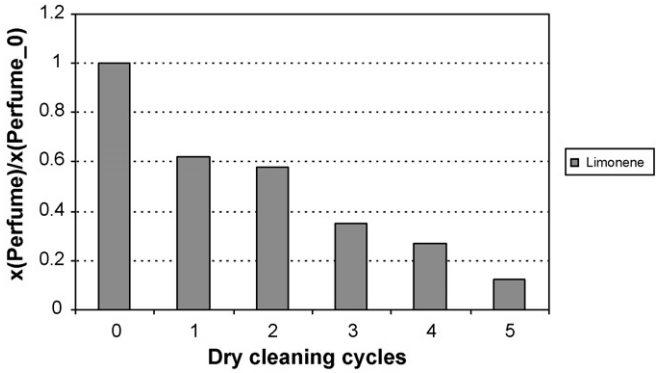

Fig. 13. Quantity of limonene present in the headspace according to the number of dry cleaning cycles.

The GC-headspace analysis of impregnated fabrics with perfume microcapsules and subjected to different abrasion cycles, namely 3000, 6000 and 9000 abrasion cycles were performed. By GC-headspace, it was determined the quantity of each component of the perfume in function of abrasion cycles. Abrasion test were performed to evaluate the resistance of fabrics. The principle of this test is to put the textile between two discs that are driven by a rotor along a zigzag course in a circular orbit so that the fabric is subjected to flexing, rubbing, shock, compression, stretching and other mechanical forces during the test. Each circular movement is a cycle. The test was carried out in a MARTINDALE apparatus according to the norm ISO 12947-2.

The effect of the number of abrasion cycles on the concentration of microencapsulated perfume in fabrics was also studied at the laboratory scale. There is still a significant amount of fragrance inside the microcapsules after 9000 cycles of abrasion, although the musk scent was not detected. The relative amounts of limonene, vetiver and jasmin scents were reduced, respectively to 78%, 59% and 50%, of the initial content.

The impregnated textile fabrics with perfume microcapsules obtained with an industrial foulard showed resistance to five dry washing cycles although the musk scent was absent as already noticed in the laboratory scale experiments; after 5 cycles vetiver was around 30% of the initial amount, jasmin scent around 60% of the initial amount and limonene was still present. The industrial impregnated fabric supported 3000 abrasion cycles but failed the test of 9000 abrasion cycles, for which no fragrance was detected. This agrees with the observed aspect of microcapsules in SEM shown in Fig. 10.

4. Conclusions

PUU microcapsules of masculine perfume were produced by interfacial polymerisation technique. The impregnation of textile fabrics with microencapsulated perfumes was studied both at laboratory and industrial scale using a foulard.

Infrared spectra of the microcapsules shell was obtained for determining isocyanate conversion. The absence of the peak at 2270 cm^{-1} confirmed that there are no residual isocyanate groups in the samples, which means that it has fully reacted.

The particle size distribution was obtained using laser dispersion technique. A bimodal size distribution in volume was observed, showing many small particles with mean particle size of 1 μm and large particles with mean particle size of 10 μm. The observation of microcapsules by optical microscopy confirmed the spherical form.

SEM micrographs have shown good adhesion between microcapsules and textile fibres, and also confirmed the spherical morphology and size. In the industrial process of impregnation it was observed a change of the microcapsules shape. Some microcapsules are broken and empty after fabric impregnation in the laboratory and are also agglomerated in the industrial process.

The encapsulation efficiency and the presence of perfume on textile substrate were quantified through GC-FID-headspace analysis. The encapsulation efficiency accounts for 55% of the loaded perfume used in the encapsulation process. Comparing each component of the perfume with their odor threshold the results showed that musk and limonene scent odor values are the highest so these are the components that we smell more.

During dry cleaning of lab-scale impregnated fabrics, the loss of limonene was 38% in the first cycle and up to 87% after five dry cleaning cycles. The industrial scale impregnated textiles also showed resistance to five dry cleaning cycles. The amount of limonene component in the fabric was compared with its threshold and the odor value was calculated confirming that there is a decrease on odor value with five dry cleaning cycles.

Acknowledgements

This work was carried out in the project SCENTFASHION, contract ADI/2004/M2.3/0015POCI funded by Agência de Inovação (AdI) in the framework of POCI 2010-Medida 2.3-IDEIA. We also acknowledge the support of our partners CITEVE and A Penteadora, SA.

References

[1] S.N. Rodrigues, I. Fernandes, I.M. Martins, V.G. Mata, F. Barreiro, A.E. Rodrigues, Microencapsulation of limonene for textile application, Ind. Eng. Chem. Res. 47 (2008) 4142.
[2] E.C. Cussler, G.D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, UK, 2001.
[3] J.A. Wesselingh, S. Kill, M.E. Vild, Design & Development of Biological, Chemical, Food and Pharmaceutical Products, Wiley, Chichester, UK, 2007.
[4] J. Wei, Product Engineering. Molecular Structure and Properties, Barnes & Noble, 2006.
[5] K. Ulrich, S. Eppinger, In Product design and development, 3rd ed.; McGraw Hill: New York, 2003.

[6] M.K. Zia, H.N. Bhatti, I.A. Bhatti, Methods for polyurethane and polyurethane composites, recycling and recovery: a review, React. Funct. Polym. 67 (2007) 675.
[7] K. Hirech, S. Payan, G. Carnelle, L. Brujes, J. Legrand, Microencapsulation of an insecticide by interfacial polymerisation, Powder Technol. 130 (2003) 324.
[8] P. Monllor, M.A. Bonet, F. Cases, Characterization of the behaviour of flavour microcapsules in cotton fabrics, Eur. Polym. J. 43 (2007) 2481.
[9] N. Gordon, Microencapsualtion in textile finishing, Rev. Prog. Coloration (2001) 321.
[10] N. Gordon, Microencapsulates in textile coloration and finishing, Rev. Prog. Coloration 21 (1991) 72.
[11] M.I. Ré, B. Biscans, Preparation of microspheres of ketoprofen with acrylic polymers by a quasi-emulsion solvent diffusion method, Powder Technol. 101 (1999) 120.
[12] S. Vasiliu, M. Popa, M. Rinaudo, Polyelectrolyte capsules made of two biocompatible natural polymers, Eur. Polym. J. 41 (2005) 923.
[13] C. Muzzarelli, V. Stanic, L. Gobbi, G. Tosi, R.A.A. Muzzarelli, Spray-drying of solutions containing chitosan together with polyuronans and characterisation of the microspheres, Carbohydr. Polym. 57 (2004) 73.
[14] K. Gniotek, Odour measurements in textile industry, Fibres Text East Eur. 11 (1) (2003) 40.
[15] T. Öktem, Surface treatment of cotton fabrics with chitosan, Color Technol. 119 (2003) 241.
[16] S. Mondal, Phase change materials for smart textiles—an overview, Appl. Thermal Eng. 28 (2008) 1536.
[17] R. Costa, G.D. Moggrifge, P.M. Saraiva, Chemical product engineering: an emerging paradigm within chemical engineering, AIChE J. 52 (6) (2006) 1976.
[18] S. Li, J.E. Lewis, N.M. Stewart, L. Qian, H. Boyter, Effect of finishing methods on washing durability of microencapsulated aroma finishing, J. Textile Inst. 99 (2) (2008) 177.
[19] Business and market analysis for the world's fibre, textile and apparel industries, Textile Intelligence, Press release 17.06.2005. http://www.textilesintelligence.com/til/press.cfm?prid=345 (accessed July 18, 2008).
[20] D.M. Whitaker, Stabilized perfume containing microcapsules and method of preparing same, U.S. Patent 5,051,305 (1991).
[21] M. Kukovic, E. Knez, Process for preparing carries saturated or coated with microencapsulated scents, WO 96/09114, 1996.
[22] J.C. Soper, Y.K. Kim, M.T. Thomas, Method of encapsulation flavours and fragrances by controlled water transport into microcapsules, U.S. Patent 6,045,835 (2000).
[23] D. Quong, Active material within hydrogel microbeads, WO 01/030145 A1, 2001.
[24] L. Harris, L. Blevins, Process for applying microcapsules to textile materials and products formed by the process, WO 02/090643 A1, 2002.
[25] M. Kleban, J. Weisser, F. Koch, W. Schwaiger, Leather finished with scent containing microcapsules, U.S. Patent 2002/0198392 A1 (2002).
[26] D. Benczedi, P. Bouquerand, E. Steinboeck, Process for the preparation of extruded delivery systems, WO 03/056938 A1, 2003.
[27] A. Bochot, H. Alphandary, D. Duchene, E. Fatal, Microencapsulation systems and applications of same, WO 04/066906 A2, 2004.
[28] J. Xing, Y. Li, E. Newton, Method for encapsulating phase transitional paraffin compounds using melamine-formaldehyde and microcapsule resulting therefrom, WO 04/058390 A1, 2004.
[29] P. Schöcker, R. Widmaier, B. Müller, D. Wulff, P. Gernert, H. Korb, Microcapsule dispersions, WO 06/048166 A1, 2006.
[30] L. Ouali, D. Benczedi, Process for producing nano-capsules containing a fragrance, WO 2006/027664 A2, 2006.
[31] L. Ouali, D. Benczedi, Polyurethane and polyurea microcapsules, WO 2007/004166 A1, 2007.
[32] J. Carles, A method of creation in perfumery, Soap Perfumes Cosmet. 35 (1962) 328.
[33] W.A. Poucher, A classification of odors and its uses, J. Soc. Cosmet. Chem. (1955) 81.
[34] W.A. Poucher, A classification of odors and its uses, Am. Perfumer Essent Oil Rev. (1955) 17.
[35] N. Gordon, Application of microencapsulation in textiles, Int. J. Pharm. 242 (2002) 55.
[36] S.K. Gosh, Functional coatings and microencapsulation: a general perspective, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006.
[37] V.G. Mata, P. Gomes, A.E. Rodrigues, Engineering perfumes, AiChE J. 51 (2005) 2834.
[38] P.B. Gomes, V.G. Mata, A.E. Rodrigues, Experimental validation of perfumery ternary diagram® methodology, AiChE J. 54 (2008) 310.
[39] Database ChemSpider™ Building a Structure Centre Community for Chemists. Available online at: www.Chemspider.com (accessed 2008).
[40] R.R. Calkin, J.S. Jellinek, Perfumery: Practice and Principles, Willey, New York, 1994.
[41] J.C. Leffingwell, Chirality and Bioactivity. I. Pharmacology, vol. 3 (no. 1), Leffingwell Reports, 2003.
[42] G. Frater, U. Mueller, P. Kraft, Purification and olfactory characterization of the enantiomerically pure isomers of the perfumery synthetic Galaxolide®, Helv. Chim. Acta 82 (10) (1999) 1656.